Magnetic Clusters

Mixed Transition-Metal—Lanthanide Complexes at Higher Oxidation States: Heteronuclear Ce^{IV}–Mn^{IV} Clusters[**]

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High oxidation-state molecular compounds or polymeric oxides of Mn or Ce have a wide range of applications in diverse areas involving inorganic, organic, environmental, and industrial chemistry owing to their ability to oxidize both inorganic and organic substrates.[1–8] The high oxidation-state tetranuclear Mn cluster that is present near photosystem II of

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green plants is responsible for the oxidation of H_2O to dioxygen.[1,2] As a result, a number of Mn_4 complexes have been made to model its structural and functional properties.[1] Ce^{IV} has also been used in the homogeneous and heterogeneous catalysis by Ru complexes of water oxidation to molecular dioxygen.[2] Similarly, MnO_4^- and Ce^{IV} are commonly employed as oxidants in inorganic synthesis, such as in the formation of Mn^{III} and/or Mn^{IV} clusters, or mixed-valent $Co^{III,IV}$ complexes.[3,4] In addition, compounds such as MnO_4^-, MnO_2, and $(NH_4)_2[Ce(NO_3)_6]$ have a long history as oxidizing agents for a vast variety of organic substrates.[5,6] Further, Mn^{III}, Mn^{IV} and Ce^{IV} oxides have been widely used, either alone or as mixed Mn/Ce oxides, in a number of heterogeneous catalytic oxidation processes.[7,8] For example, Ce^{IV}/Mn^{IV} composite oxides are being widely used in sub- and supercritical catalytic wet oxidations for the treatment of wastewater containing toxic organic pollutants such as ammonia, acetic acid, pyridine, phenol, polyethylene glycol, and others.[8] Mixed Ce^{IV}/Mn^{IV} molecular analogues of these Ce/Mn oxide catalysts have not been available for study, but would likely prove to have interesting oxidative and other properties. We herein report the synthesis, crystallographic characterization and magnetic properties of a novel family of mixed Ce^{IV}/Mn^{IV} complexes with various Ce:Mn ratios. These are also the first crystallographically characterized molecular Mn/Ce complexes in general.

The new compounds described below were all obtained as part of a larger investigation of the oxidation of Mn^{II} reagents by Ce^{IV} under a variety of conditions. The reaction of $Mn(NO_3)_2\cdot xH_2O$ and 2,2′-bipyridine (bpy) with $(NH_4)_2[Ce(NO_3)_6]$ in a 1:1:2 molar ratio in 25% aqueous acetic acid gave $[Ce^{IV}Mn^{IV}_2O_3(O_2CMe)(NO_3)_4(H_2O)_2(bpy)_2](NO_3)\cdot 2H_2O$ (**1**$\cdot 2H_2O$) in 40% yield. Similarly, the reaction of $[Mn(O_2CMe)_2]\cdot 4H_2O$ and 6-methyl-2-hydroxypyridine (mhpH)[9] with $(NH_4)_2Ce(NO_3)_6$ in a 4:9:6 molar ratio in 30% aqueous acetic acid gave $[Ce_3Mn_2O_6(O_2CMe)_6(NO_3)_2(mhpH)_4]\cdot 2H_2O$ (**2**$\cdot 2H_2O$) in 24% yield. Finally, the reaction of a solution of $[Mn(O_2CMe)_2]\cdot 4H_2O$ in 50% aqueous acetic acid with $Ce(ClO_4)_4$ (0.5 M solution in $HClO_4$) in a 2:3 molar ratio gave $[Ce^{IV}Mn^{IV}_6O_9(O_2CMe)_9(MeOH)(H_2O)_2](ClO_4)\cdot 3H_2O\cdot \tfrac{1}{2}MeCO_2H$ (**3**$\cdot 3H_2O\cdot \tfrac{1}{2}MeCO_2H$) in ≈50% yield. Charge considerations, inspection of metric parameters and bond valence sum calculations establish that all the Ce and Mn ions of **1**–**3** are in oxidation state IV.[10]

The structure of the cation of **1** (Figure 1)[11] comprises a $[Mn^{IV}_2(\mu\text{-}O)_2(\mu\text{-}O_2CMe)]^{3+}$ rhomb linked to a Ce^{IV} ion through a linear oxide bridge. The Mn-Mn-Ce angle is 139.6(2)°. The ten-coordinate Ce^{IV} ion is additionally ligated by four bidentate nitrate groups and a water molecule. Octahedral coordination at each Mn is completed by a chelating bpy group and a terminal water molecule at Mn2. The Mn−O and Mn−N bond lengths, and the Mn⋅⋅⋅Mn separation (2.659 Å) are typical of those in discrete dinuclear complexes containing the $[Mn^{IV}_2(\mu\text{-}O)_2(\mu\text{-}O_2CMe)]^{3+}$ core.[4a] The Ce−O bond lengths (2.44–2.60 Å) are slightly longer than is typical for ten-coordinate Ce^{IV} (Ce−O bond lengths ≈2.3–2.5 Å),[10c] probably as a consequence of the very short Ce^{IV}−O^{2-} bond (Ce−O5 = 1.945 Å), one of the shortest Ce−O bond lengths ever reported. Complex **1** is a new structural type for a mixed Tr/Ln complex (where Tr = transition metal, Ln = lanthanide).

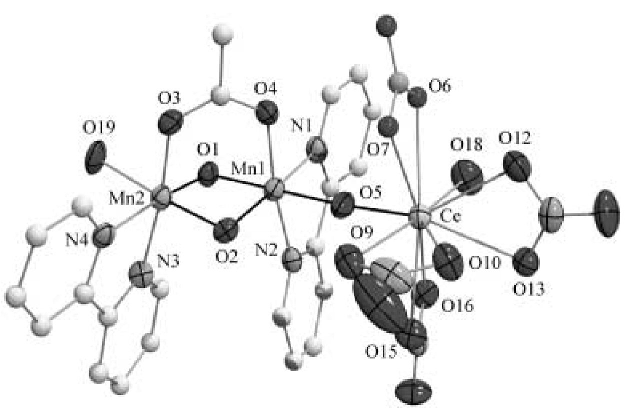

Figure 1. The cation of complex **1**, labeled ORTEP plot (at the 50% probability level) in PovRay format.

The structure of **2** (Figure 2, top)[11] consists of a Ce^{IV}_3 isosceles triangle, each edge of which is bridged by two μ_3-O^{2-} ions that also bridge to the two Mn^{IV} ions lying one each above and below the Ce^{IV}_3 triangle forming an M_5 trigonal bipyramid (Mn⋅⋅⋅Mn = 4.818 Å), (Figure 2, bottom).[12] Peripheral ligation is completed by bridging acetate,[12] chelating nitrate and terminal mhpH groups, the latter

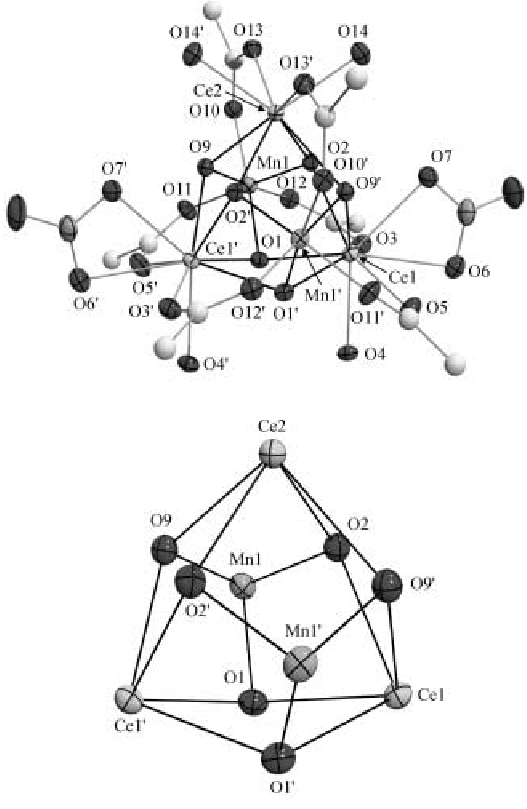

Figure 2. Top: Complex **2**, the methylpyridine groups are omitted, labeled ORTEP plot (at the 50% probability level) in PovRay format. Bottom: The $[Ce^{IV}_3Mn^{IV}_2O_6]^{8+}$ core of **2** emphasizing its trigonal bipyramidal topology.

protonated at their N atoms and binding only through their O atoms (O4 and O14). The molecule has crystallographically imposed C_{2v} symmetry, the C_2 axis passing through Ce2 and bisecting the O1···O1′ vector. The Ce–O bond lengths are within the expected range for octa- and enneacoordinate Ce^{IV}.[10c] The Ce_3Mn_2 trigonal bipyramidal topology has been observed in mixed 4f/3d chemistry only once before, in a $Nd^{III}_3Cr^{III}_2$ complex that contains hydroxide bridges, rather than oxide ones as in **2**.[12a]

The structure of **3** (Figure 3, top)[11] contains an unprecedented Mn^{IV}_6 wheel. Its edges are bridged alternately by $(\mu_2\text{-O})(\mu_3\text{-O})(\mu\text{-}O_2CMe)$ and $(\mu_3\text{-O})(\mu\text{-}O_2CMe)_2$ ligand sets, with Mn···Mn separations of 2.714 and 3.297 Å, respectively. The μ_3-O^{2-} ions are those holding in place the central Ce^{IV} ion,[12] which lies slightly out of the almost planar Mn_6 ring and is also coordinated to one MeOH and two water groups. The Ce–O bond lengths (2.271–2.483 Å) are within the expected range for enneacoordinate Ce^{IV}.[10c] The Mn^{IV}-O^{2-} (1.794–1.863 Å) and Mn–O (acetate) bond lengths (1.931–1.975 Å) are typical of Mn^{IV} values. Apart from being the first Mn^{IV}_6 wheel, complex **3** is also the first Mn^{IV} complex with only oxide and carboxylate ligands, and its $[M_7O_9]$ core (Figure 2, bottom) is of a structural type never seen before for any metal. In addition it is one of the few known examples of a cyclic Tr_6Ln complex, that is, a wheel of transition-metal ions with a central lanthanide ion.[13]

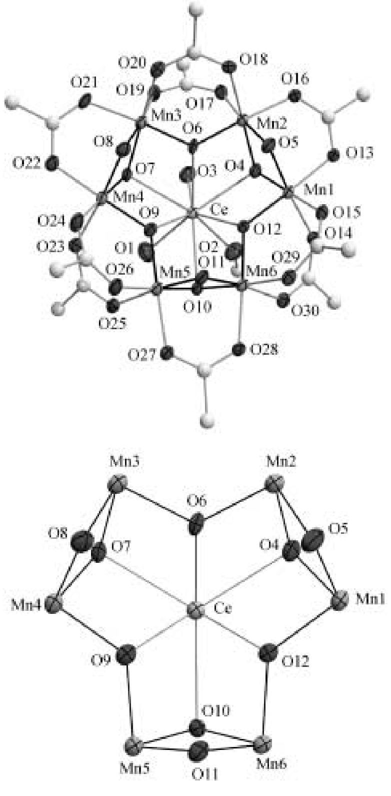

Figure 3. Top: Complex **3**, labeled ORTEP plot (at the 50% probability level) in PovRay format. Bottom: The $[Mn^{IV}_6Ce^{IV}O_9]^{10+}$ core of **3**.

Solid-state, magnetic susceptibility measurements were carried out on complexes **1**–**3** in the temperature range 5.0–300 K in a 10 kG dc magnetic field. The obtained data are shown as χ_MT versus T plots (Figure 4; χ_M is the magnetic susceptibility). All paramagnetism is associated with the Mn^{IV} ions, since Ce^{IV} is diamagnetic (f^0). The data for **1** and **2** were fit to the theoretical χ_MT vs. T expression for a d^3–d^3 dimer.[14] The fits (solid lines in Figure 4) gave $J = -45.7\ cm^{-1}$, $\rho = 0.019$, and $g = 1.95$ for **1**, and $J = -0.40\ cm^{-1}$, $\rho = 0.010$, and $g = 2.01$ for **2**, J is the exchange interaction constant, and ρ is the fraction of paramagnetic impurity (assumed to be high-spin Mn^{II}). A temperature independent paramagnetism (TIP) term was held constant at $300\times10^{-6}\ cm^3 mol^{-1} K$ for **1**, and $500\times10^{-6}\ cm^3 mol^{-1} K$ for **2**.[15] The data for **3** were fit by a matrix diagonalization method described elsewhere.[16] Three exchange constants were used as parameters, J_1 and J_2 for the $[Mn^{IV}_2O_2(O_2CMe)]$ and $[Mn^{IV}_2O(O_2CMe)_2]$ units, respectively, and J_3 for a uniform next-nearest-neighbor interaction. The preliminary fit (solid line in Figure 4) using data above 25 K to avoid intermolecular interactions gave $J_1 = -5.8\ cm^{-1}$, $J_2 = -0.63\ cm^{-1}$, $J_3 \approx 0$, $\rho = 0.0299$, and $g = 2.07$, with TIP held constant at $700\times10^{-6}\ cm^3 mol^{-1} K$.[15]

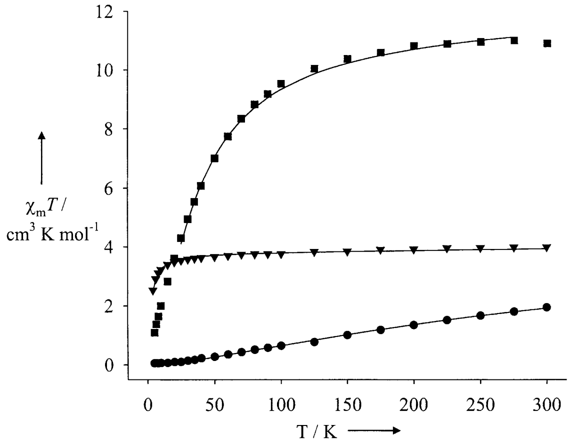

Figure 4. χ_MT versus T plot for complexes **1** (●), **2** (▼) and **3** (■). The solid lines are the fits of the data; see the text for the fit parameters.

Complexes **1**–**3** are thus all antiferromagnetically coupled with $S = 0$ ground states. The J value for **1** is in agreement with previously reported values (-24.6 to $-67\ cm^{-1}$) for dinuclear complexes with a $[Mn^{IV}_2(\mu\text{-O})_2(\mu\text{-}O_2CMe)]$ core.[4a,17] The J value for **2** is very weak, as expected for two well separated Mn^{IV} ions interacting through four-bond superexchange pathways. The J_1 value gauging the interaction within the $[Mn^{IV}_2O_2(\mu\text{-}O_2CMe)]$ units of **3** is significantly smaller than the lower limit of the above range for dinuclear complexes. This is consistent with the attachment of the strongly Lewis acidic Ce^{4+} ion, which weakens the Mn–O^{2-} bonds that mediate the Mn^{IV}_2 superexchange interaction. This is reflected in the significantly longer Mn–(μ_3-O^{2-}) bond lengths [av 1.859 Å] and Mn···Mn separations [av 2.714 Å] in this unit in **3**, compared with the Mn–(μ-O^{2-}) bonds of **3** [av 1.813 Å], and the Mn···Mn distances [range 2.58–2.67 Å] of dinuclear compounds containing the $[\mathrm{Mn^{IV}_2(\mu\text{-}O)_2(\mu\text{-}O_2CMe)}]$ core.[4a] The very small J_2 value can also be rationalized on the basis of the long $\mathrm{Mn{-}(\mu_3\text{-}O^{2-})}$ bond lengths [1.83 Å] and Mn···Mn separations [3.297 Å], although discrete dinuclear complexes containing the $[\mathrm{Mn^{IV}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2}]$ core are currently unknown and thus unavailable for comparison.

The described results establish synthetic access to a new class of mixed $\mathrm{Ce^{IV}/Mn^{IV}/O^{2-}}$ molecular clusters. Although there are a few other reported examples of high oxidation state, mixed transition-metal/lanthanide complexes containing early transition-metal ions such as $\mathrm{Ti^{IV}}$ or $\mathrm{Nb^{V}}$,[12f] compounds **1**–**3** are unique in that both component ions are strong oxidizing agents. The species obtained to date already span a wide range of Ce:Mn ratios, from 3:2 (**2**), 1:2 (**1**), to 1:6 (**3**), and others will undoubtedly be possible. It is interesting that **1**–**3** all contain $\mathrm{Ce^{IV}}$ even though $\mathrm{Ce^{IV}}$ was used as the oxidant of $\mathrm{Mn^{II}}$ in the reaction, and the $\mathrm{Mn^{II}}$:$\mathrm{Ce^{IV}}$ reaction ratios were such that all $\mathrm{Ce^{IV}}$ was ostensibly reduced to $\mathrm{Ce^{III}}$ in generating $\mathrm{Mn^{IV}}$. We believe that this is more than happenstance: The generation of high oxidation state $\mathrm{Mn^{IV}}$ is known to favor formation of non-mononuclear products containing bridging $\mathrm{O^{2-}}$ ions, but the presence of the hard $\mathrm{O^{2-}}$ ions will also in turn favor incorporation of hard $\mathrm{Ce^{4+}}$ ions, facilitating formation of $\mathrm{Ce^{IV}/Mn^{IV}}$ products, which perhaps involves the participation of atmospheric oxygen. Complexes **1**–**3** have unusual and aesthetically pleasing structures, but they are also soluble in organic solvents, thus making them valuable starting materials for further synthesis and reactivity studies. In particular, their solubility and the high oxidative strength of the metal ions they contain make them very attractive new candidates for catalytic and noncatalytic oxidation of a variety of organic and inorganic substrates.

Experimental Section

1·$2\,H_2O$: An orange solution of $\mathrm{(NH_4)_2[Ce(NO_3)_6]}$ (5.50 g, 10.03 mmol) in $\mathrm{H_2O/MeCO_2H}$ (19 ml/7 ml) was slowly added to a pale yellow-brown solution of $\mathrm{Mn(NO_3)_2{\cdot}\mathit{x}H_2O}$ (0.90 g, 5.03 mmol) and bpy (0.78 g, 5.00 mmol) in $\mathrm{H_2O/MeCO_2H}$ (50 ml/16 ml) resulting in a dark greenish-brown solution. The solution was reduced in volume by ≈60% by rotary-evaporation at 40°C, and then maintained undisturbed at ambient temperature. After 24 h, dark greenish-brown crystals were collected by filtration, washed with cold acetone (2 × 7 mL) and $\mathrm{Et_2O}$ (2 × 15 ml), and dried in vacuo. The yield was 1.06 g (40% based on Mn). Elemental analysis calcd (%) for $\mathrm{C_{22}H_{27}N_9O_{24}CeMn_2}$ (**1**·$2\,H_2O$): C 25.13, H 2.59, N 11.99; found: C 25.21, H 2.32, N 11.70. Selected IR data (KBr pellet): $\tilde{\nu} = 3400$(s, br), 1602(m), 1560(w), 1498(m), 1470(m), 1446(s), 1384(s), 1310(s), 1286(m), 1170(w), 1158(w), 1107(w), 1073(w), 1060(w), 1035(m), 825(w), 811(w), 772(s), 738(w), 715(m), 693(w), 670(m), 655(m), 630(s), 592 (m), 419(w) $\mathrm{cm^{-1}}$.

2·$2\,H_2O$: An orange solution of $\mathrm{(NH_4)_2[Ce(NO_3)_6]}$ (6.78 g, 12.37 mmol) in $\mathrm{H_2O/MeCO_2H}$ (9 mL/5 mL) was slowly added to a pale yellow-brown solution of $\mathrm{Mn(O_2CMe)_2{\cdot}4\,H_2O}$ (2.02 g, 8.24 mmol) and mhpH (2.00 g, 18.33 mmol) in $\mathrm{H_2O/MeCO_2H}$ (6 mL/1.5 mL) resulting in a dark reddish-brown solution. This was allowed to slowly evaporate at ambient temperature, and after a few days the now dark-red solution had started to produce dark red crystals. After several more days, the formation of large well-shaped red crystals was judged to be complete, and they were collected by filtration, washed with 2 × 6 mL each of cold acetone and $\mathrm{Et_2O}$, and dried in vacuo. The yield was 1.15 g (24% based on Ce). Elemental analysis calcd (%) for $\mathrm{C_{36}H_{50}N_6O_{30}Ce_3Mn_2}$ (**2**·$2\,H_2O$): C 27.41, H 3.20, N 5.33; found: C 27.60, H 3.00, N 5.05. Selected IR data (KBr pellet): $\tilde{\nu} = 3431$(s, br), 3256(m), 3100(w), 2931(m), 1635(s), 1618(s), 1542(s), 1417(s), 1384(s), 1349(m), 1292(m), 1165 (m), 1028(m), 1004(m), 804(m), 745(m), 669 (m), 623 (s), 610(s), 578(s), 505(m), 490(m), 438(m) $\mathrm{cm^{-1}}$.

3·$3\,H_2O{\cdot}0.5\,HO_2CMe$: An orange mixture of a 0.5 M solution in $\mathrm{HClO_4}$ of $\mathrm{Ce(ClO_4)_4}$ (12.3 mmol, 24.6 mL) and a few drops of MeOH (≈0.2 mL) was slowly added to a colorless solution of $\mathrm{Mn(O_2CMe)_2{\cdot}4\,H_2O}$ (2.02 g, 8.24 mmol) in $\mathrm{H_2O/MeCO_2H}$ (4 mL/4 mL). The resulting dark reddish-brown solution was maintained at room temperature for about a week. The black crystals that formed were then collected by filtration, washed with ≈5 mL each of cold acetone and $\mathrm{Et_2O}$, and dried in vacuo. The yield was 0.70 g (49% based on Ce). Elemental analysis calcd (%) for $\mathrm{C_{20}H_{43}O_{38}ClCeMn_6}$ (**3**·$3\,H_2O{\cdot}\tfrac{1}{2}MeCO_2H$): C 17.20, H 3.10; found: C 16.90, H 3.00. Selected IR data (KBr pellet): $\tilde{\nu} = 3421$(s, br), 1635(w), 1555(s), 1493(m), 1421(s), 1352(m), 1144(m), 1110(s), 1090(s), 1046(m), 1030(m), 951(w), 746(m), 693(m), 668(m), 628(s), 500(m) $\mathrm{cm^{-1}}$.

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